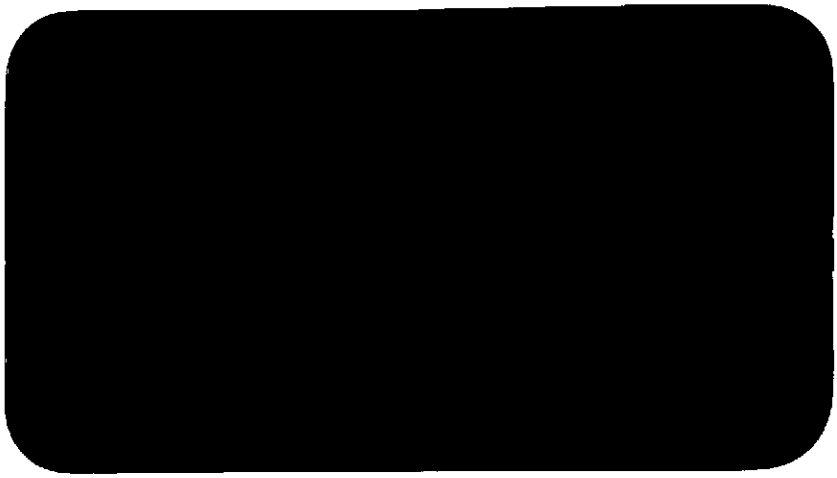

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Contract No. NAS8-26791
Report No. IITRI-C6233-40
(Triannual Report)

DEVELOPMENT OF SPACE STABLE THERMAL CONTROL COATINGS FOR USE ON LARGE SPACE VEHICLES

National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Huntsville, Alabama 35812

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January 1 through April 31, 1974

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114-03-51-0000-33-2-004-080-2510

August, 1974

FOREWORD

This is Report No. IITRI-C6233-40 (Triannual Report) of IITRI Project C6233, Contract No. NAS8-26791, entitled "Development of Space Stable Thermal Control Coatings for Use on Large Space Vehicles." This report covers the period from January 1 through April 31, 1974.

Major contributors to the program during this period include: Mr. J.E. Gilligan, Project Leader; Mr. Y. Harada and Mr. W. Logan, pigment manufacturing studies; Mr. F.O. Rogers, paint preparation; Messrs A. Lackland and J. Brzuskiewicz, Irradiation experiments and reflectance measurements; and Dr. A.M. Stake, general consultation and administrative management.

The work reported herein was performed under the technical direction of the Space Sciences Laboratory of the George C. Marshall Space Flight Center; Mr. Daniel W. Gates acted as the Project Manager.

This contract was funded under Codes 124-09-31-0000-33-1-004-080-2510 and 114-03-51-0000-33-2-004-080-2510.

Respectfully submitted,
IIT RESEARCH INSTITUTE

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ABSTRACT

The effort toward the development of a large scale manufacturing method for the production of a stable zinc orthotitanate pigment has been continuing. During this period major emphasis has been placed on the evaluation of the radiation stability of Tektronix, Inc. pigments and of the conditions (time and temperature) leading to high reflection and high optical stability. Paints were formulated in OI-650 and in OI-650G vehicles from pigments which had been prepared at various temperatures, some of which were chemically treated to remove ZnO. Ultraviolet irradiation tests of these paints were performed, and observations made regarding optimum pigment preparation parameters.

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DEVELOPMENT OF SPACE STABLE THERMAL CONTROL COATINGS FOR USE ON LARGE SPACE VEHICLES

1. INTRODUCTION

The research effort in passive spacecraft temperature control has, historically, been concentrated on the development of the class of surfaces known as solar reflectors - that is, surfaces with high reflectance for solar radiation and with high emittance in the thermal (infrared) spectrum. Basically, these surfaces must be stable in the total environment that they will experience. This requirement means that, once an high level of intrinsic stability in these materials is attained in the laboratory, we must make certain that this stability is preserved in a scaled-up process in manufacturing, protected throughout the entire pre-launch environment, and, finally, that this stability obtains in the space environment. Applications on large space vehicles, therefore, present new R&D problems - not simply traditional ones in greater dimensions.

The program consists of four major tasks: pigment manufacturing development, binder development, environmental effects evaluations, and general coatings investigations. The relative emphasis on each of these tasks varies according to the urgency of the problems elucidated in our investigations, and, of course, with the availability of time and funds. Our present efforts have been expended approximately equally on the development of a pigment manufacturing method and on the complementary environmental testing and evaluation activities.

2.0 PIGMENT DEVELOPMENT STUDIES

Studies were conducted on the decomposition behavior of coprecipated (COP) oxalates and mixed (MOX) oxalates as precursor materials in the preparation of zinc orthotitanate. In addition, zinc orthotitanate pigments were prepared for evaluation in ultraviolet space simulation studies.

2.1 Decomposition Studies

The objective of these studies was to determine whether the particle size of the precursor oxalates and the Zn_2TiO_4 product obtained from their calcination, could be controlled. The parameters investigated were calcination temperature and time of pretreatments of the COP material and of the MOX material. The various powders were processed as follows:

1) Control - oxalate mixture as coprecipitated, filtered and dried (designated LH-103).

2) Homogenized - LH-103 ground-mixed using porcelain mortar and pestle to improve mix uniformity and to reduce agglomeration (LH-103H).

3) Compacted - LH-103H compacted into one inch diameter discs under 5000 psi to reduce agglomeration and enhance particle-to-particle intimacy (LH-103C).

4) Mixed oxalates - porcelain ball-milling of a mixture (to yield a 2.05 ZnO:1.00 TiO_2 mol ratio) of individually precipitated zinc oxalate and titanium oxalate (MOX).

Samples of these four sets of materials were calcined at 600°C for 10 minutes, 1 hour, and 2 hours, by the flash calcine process, i.e., direct insertion into the furnace at temperature followed by removal after the prescribed time period. In addition, samples of each set were flash calcined at 1050°C for complete conversion to zinc orthotitanate.

The results of these studies are shown in Table 1. The weight losses for the different series calcined for 2 hours at 600°C were quite similar, i.e., 53.6%(LH-103), 53.6%(LH-103H), 53.7%(LH-103C), and 53.8%(MOX). Since the MOX series samples were also carefully weighted to yield a 2.05 ZnO:1.00 TiO_2 mixture, these weight loss data suggest a close approach to this ratio for the coprecipitated materials.

The various products were examined using X-ray powder pattern techniques to determine compositions. Among the coprecipitated materials fired at 600°C, the results showed the presence of zinc orthotitanate only in the compacted sample fired for 2 hours (LH-103C(6/2)). The higher reactivity shown for this sample was probably due to the greater intimacy between particles resulting from compaction. Previous studies conducted at 700° and 800°C with the coprecipitated powder have shown the formation of Zn_2TiO_4 at these temperatures, suggesting the reaction threshold for COP materials to be somewhere between 600° and 700°C for a 2 hour flash calcination.

Interestingly, the mixed oxalate samples in which particle intimacy might be assumed to be poorer than in a coprecipitated material, showed better reactivity at 600°C as seen by the results for MOX(6/1) and MOX(6/2). The reason for this greater reactivity may be due to a finer particle size for the MOX as compared to the COP materials. This is discussed in the next section describing scanning electron microscopy (SEM) results.

X-ray studies revealed that all of the materials fired at 1050°C had converted fully to Zn_2TiO_4. There was no evidence of any free ZnO, TiO_2 or $ZnTiO_3$.

TABLE I

SUMMARY OF CALCINATION STUDIES COMPARING COP AND MOX MATERIALS

SAMPLE	CALCINATION		% WT. LOSS	PHASES PRESENT
	Temp, °C	Time, min		
LH-103(6/.17)	600	10	53.46	$ZnO + TiO_2$
LH-103(6/1)	600	60	53.36	$ZnO + TiO_2$
LH-103(6/2)	600	120	53.59	$ZnO + TiO_2$
LH-103(6-10.5)	1050	120	-	Zn_2TiO_4
LH-103H(6/.17)	600	10	53.25	$ZnO + TiO_2$
LH-103H(6/1)	600	60	53.47	$ZnO + TiO_2$
LH-103H(6/2)	600	120	53.59	$ZnO + TiO_2$
LH-103H(6-10.5)	1050	120	-	Zn_2TiO_4
LH-103C(6/.17)	600	10	53.33	$ZnO + TiO_2$
LH-103C(6/1)	600	60	53.61	$Zno + TiO_2$
LH-103C(6/2)	600	120	53.65	$ZnO + TiO_2 + Zn_2TiO_4$ (faint)
LH-103C(6-10.5)	1050	120	-	Zn_2TiO_4
MOX(6/.17)	600	10	53.52	$ZnO + TiO_2$
MOX(6/1)	600	60	53.77	$ZnO + TiO_2 + Zn_2TiO_4$ (moderate)
MOX(6/2)	600	120	53.80	$ZnO + TiO_2 + Zn_2TiO_4$ (moderate)
MOX(6-10.5)	1050	120	-	Zn_2TiO_4

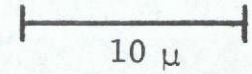
2.2 SEM Evaluation

The various precursors and calcined products were examined using the SEM. The homogenization procedure does not appear to change substantially the morphology as seen from the SEM views of LH-103 and LH-103H in Figure 1. On the other hand, the MOX material exhibited a finer particle size as seen in Figure 2. Also shown in this figure are the individual oxalates which appear somewhat coarser than after mixing (MOX). This suggests that the ball milling did cause attrition, probably in the breakup of agglomerates

Examination of calcined materials shows that the particle size difference between COP and MOX precursor materials is reflected in the 600°C decomposition products. The microstructure of LH-103(6/2) and LH-103H(6/2) (Figure 3) are similar as was the case for their precursors (Figure 1). The appearance of LH-103C(6/2) is similar to that for the other LH-103-based materials. The major departure is the microstructure of MOX (6/2) shown in Figure 4; the particle size of this material is significantly less than that of the COP-based materials. These particle size relationships also carry over to the Zn_2TiO_4 powders produced at 1050°C as seen in Figures 5 and 6. The greater reactivity observed at 600°C for MOX may have resulted from the fine particle size/high surface area nature of the MOX.

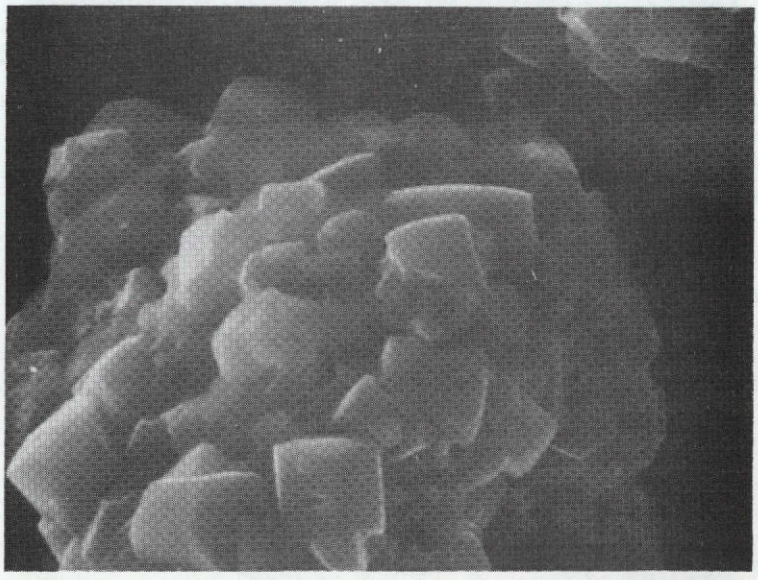
2.3 Pigment Processing for Space Simulation Studies

Zinc orthotitanate pigment materials were prepared and submitted for encapsulation testing and paint formulation. The grid to be examined is as follows:



317 3000 X

LH-103



318 3000 X

LH-103H

Figure 1. SEM VIEWS OF COP MATERIALS LH-103 and LH-103H

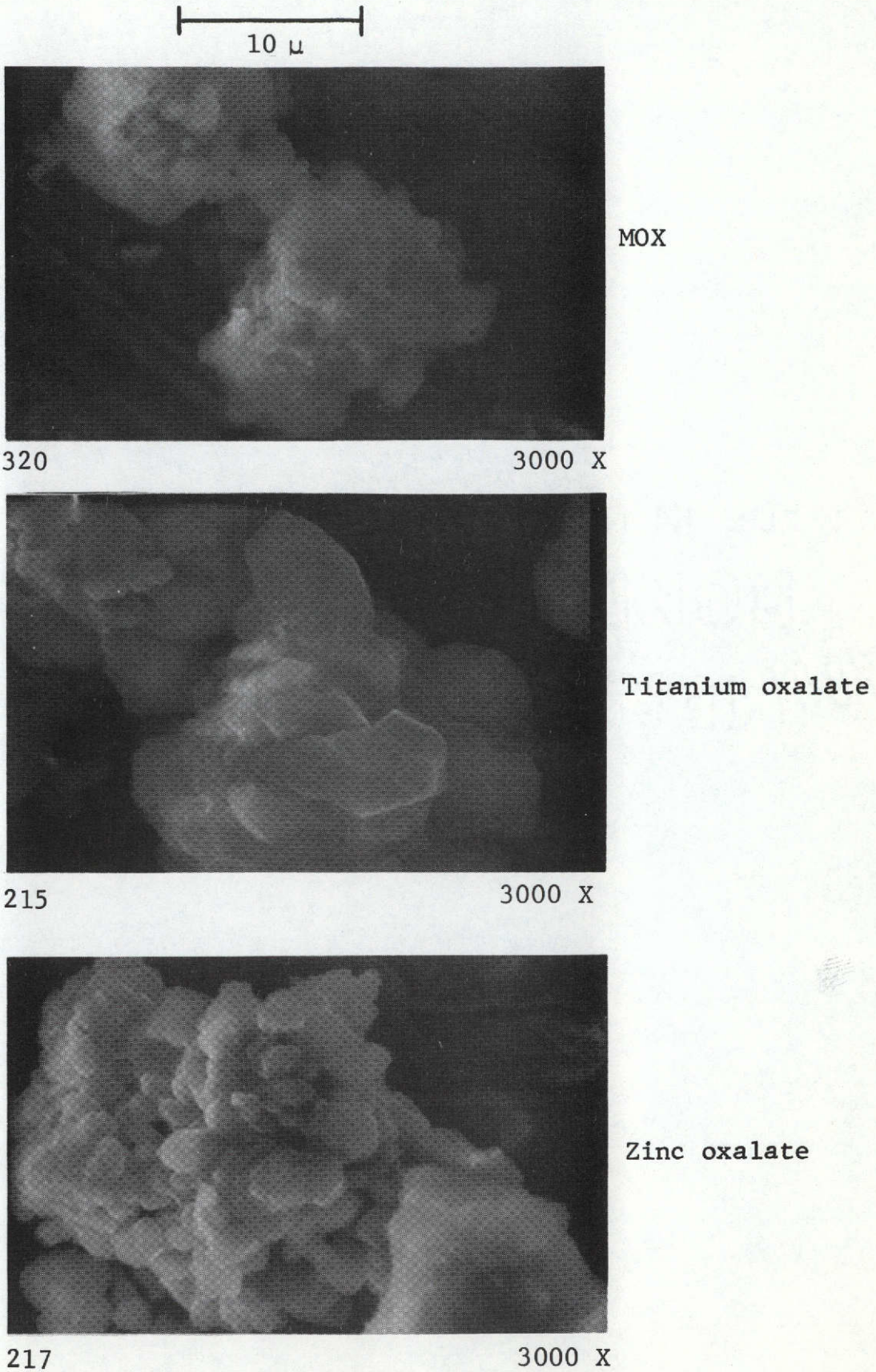
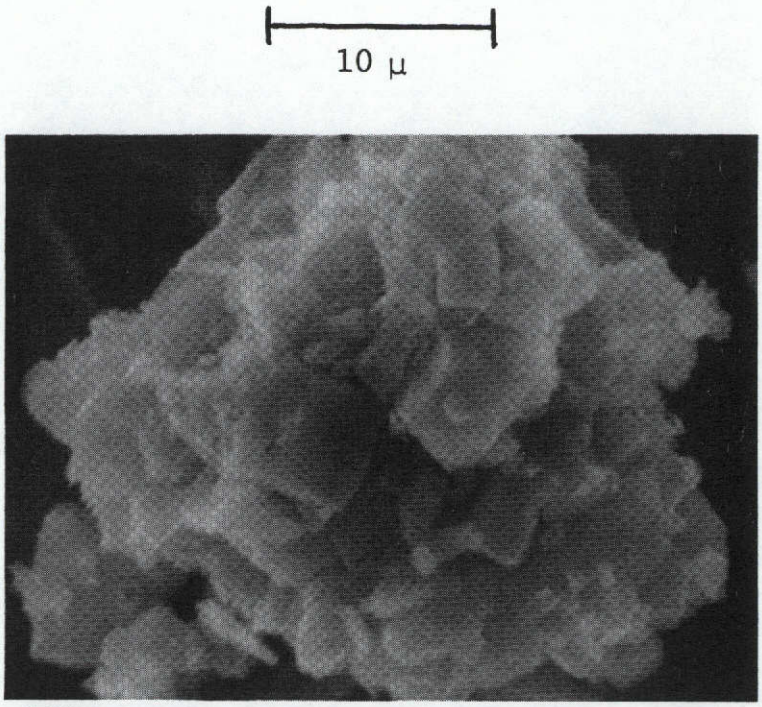
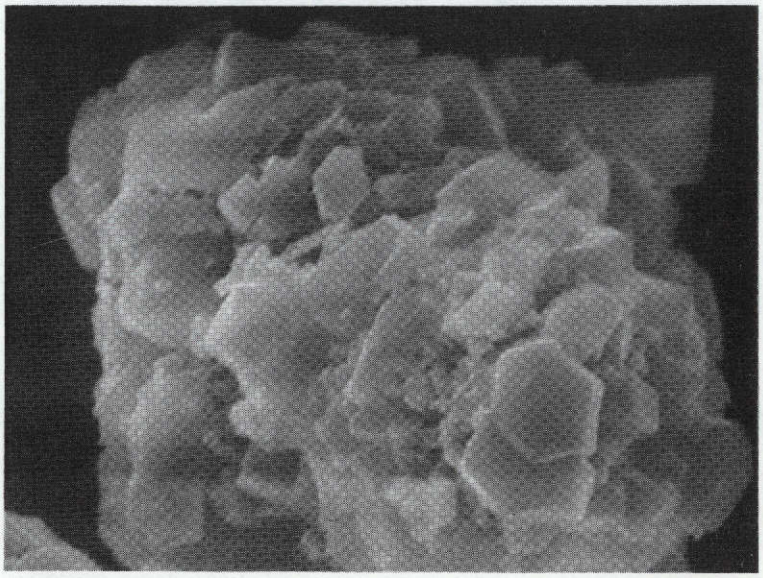


Figure 2. SEM VIEWS OF MOX MATERIAL AND INDIVIDUAL OXALATES



310 3000 X

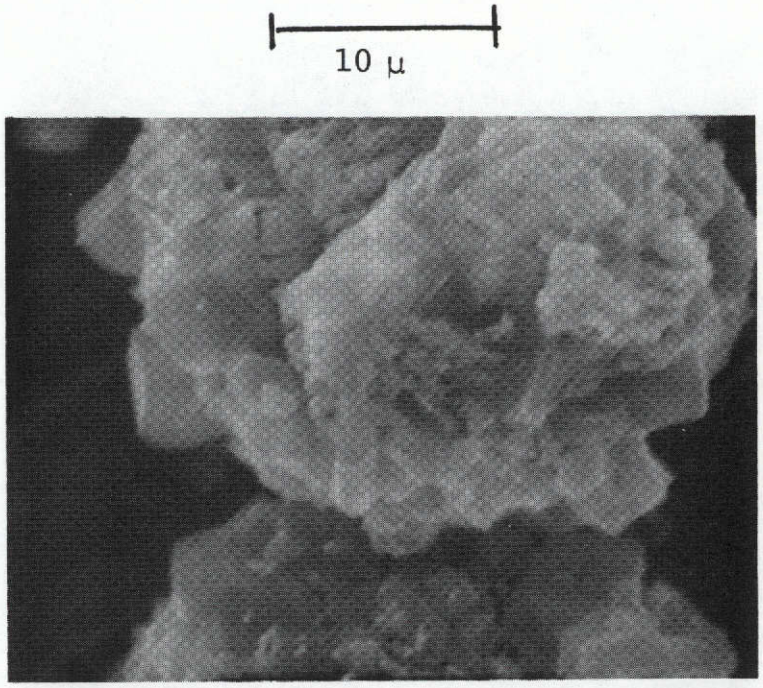
LH-103 (6/2)



312 3000 X

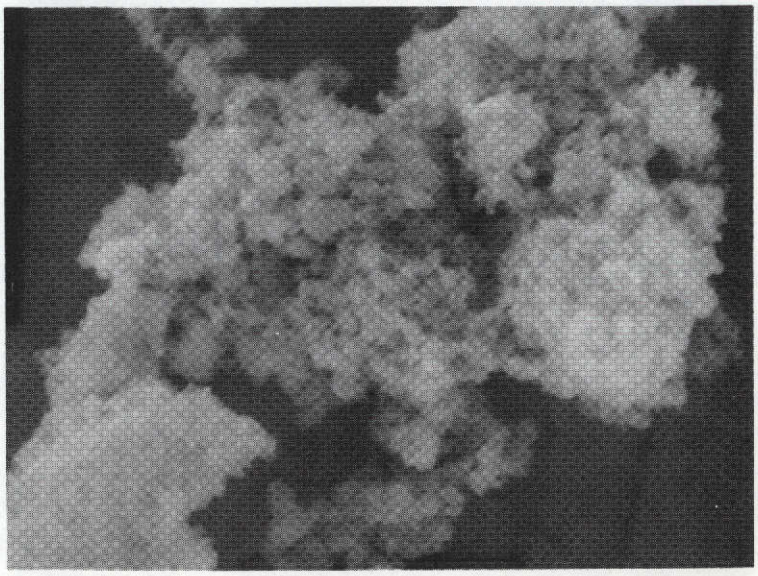
LH-103H (6/2)

Figure 3. SEM VIEWS OF COP MATERIALS CALCINED AT 600°C FOR 2 HOURS



313 3000 X

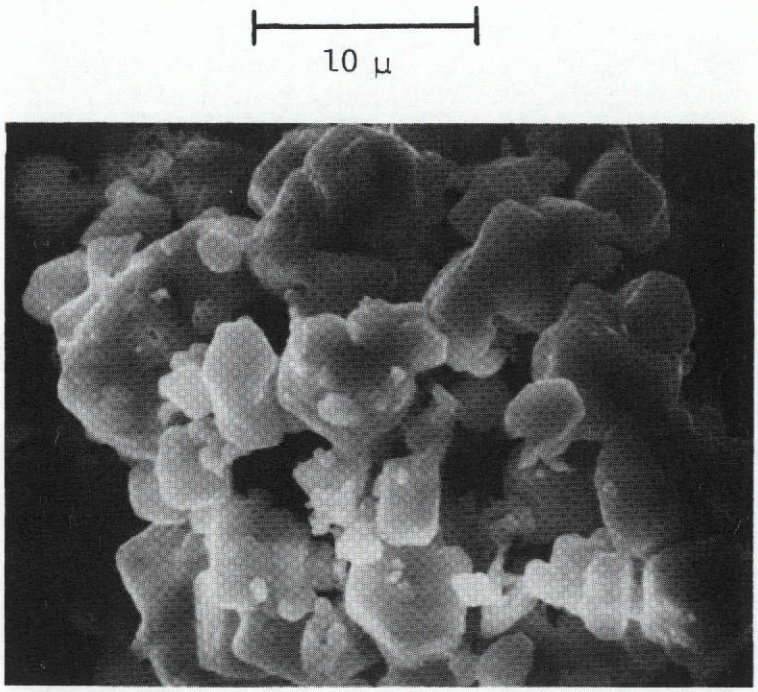
LH-103C (6/2)



322 3000 X

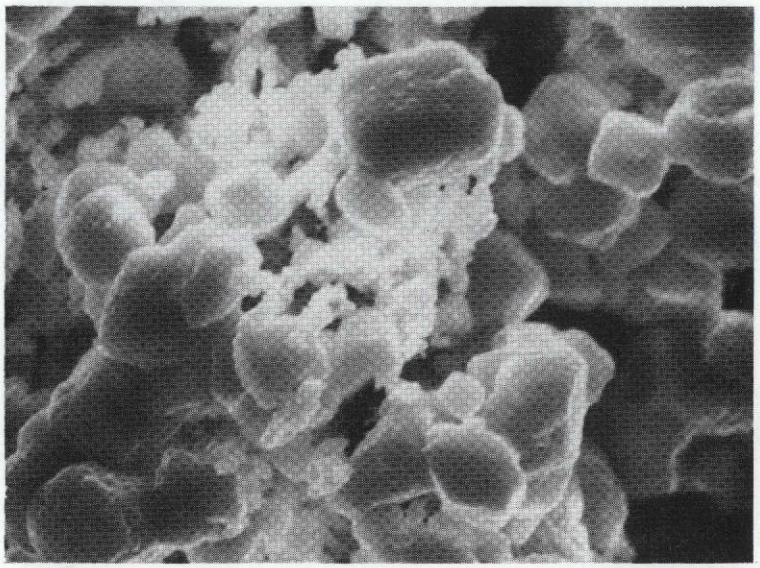
MOX (6/2)

Figure 4. SEM VIEWS OF COMPACTED COP AND MOX MATERIALS CALCINED AT 600°C FOR 2 HOURS



366 3000 X

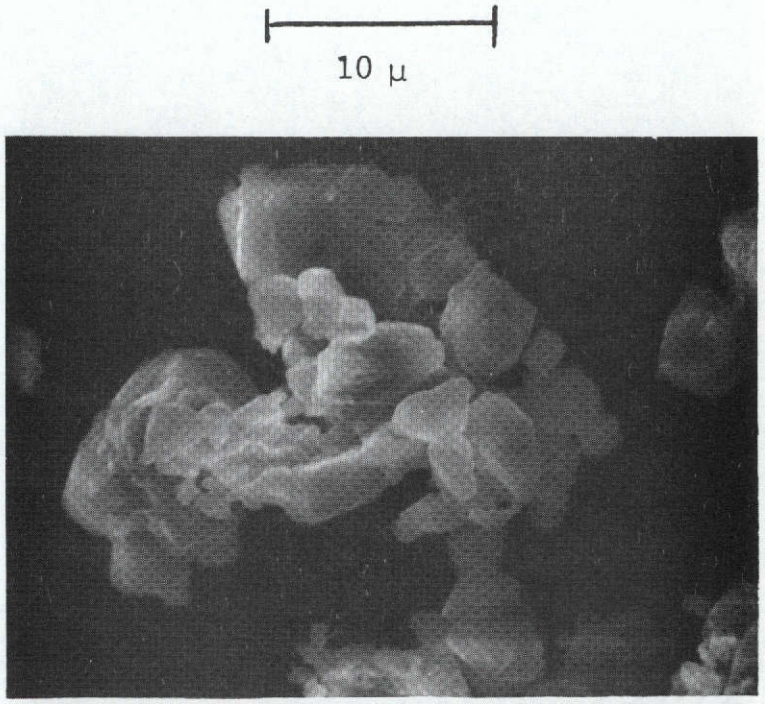
LH-103 (6-10.5)



368 3000 X

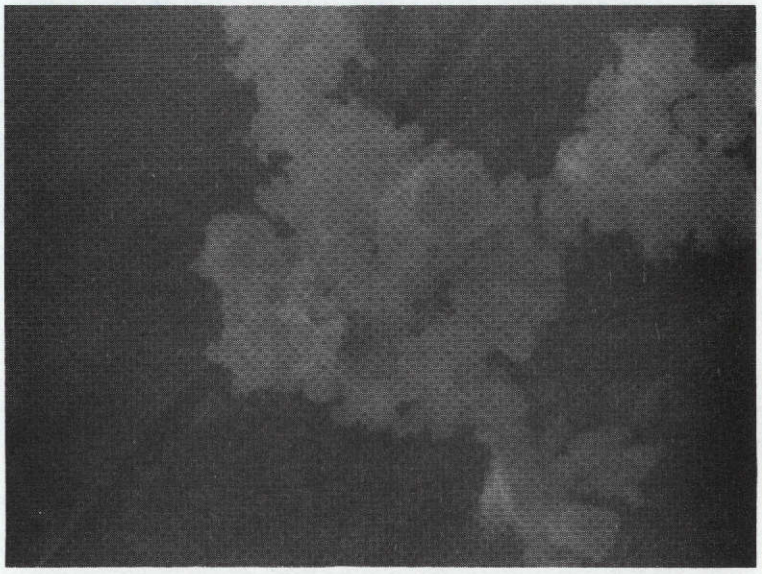
LH-103H (6-10.5)

Figure 5. SEM VIEWS OF COP MATERIALS CALCINED AT 1050°C FOR 2 HOURS



367 3000 X

LH-103C (6-10.5)



419 3000 X

MOX (6-10.5)

Figure 6. SEM VIEWS OF COMPACTED COP AND MOX MATERIALS CALCINED AT 1050°C FOR 2 HOURS

PIGMENT	ENCAPSULANT
1. LH-105(6-12)	a. None
2. LH-105(6-12-10)	b. Lithium silicate
3. LH-105(6-12-A-10)	c. Potassium silicate
	d. Potassium silicofluoride

Approximately 400 grams of each of the pigments were prepared, thus providing 100 grams for each of the 12 combinations. This total amount of 1200 grams was to provide enough material for encapsulation, formulation into paint using OI-650G, preparation of coatings for testing in ultraviolet/vacuum, and for paint storage experiments.

2.4 Conclusions

It is readily apparent from these and other studies that MOX pigments generally have a significantly smaller particle size than do COP pigments. The reason for this difference, however, is not clear; but it quite probably relates to the ball milling and to the much shorter holding times employed in the MOX process. It is important to note, however, that the COP process does indeed produce a consistent and uniform product, and that not enough is known about the MOX process to establish its reproducibility characteristics.

The ability to control the particle size of the Zn_2TiO_4 pigment has been clearly demonstrated; evidently this control resides in the ability to control the particle size of the precursor materials, the final particle size being very definitely related to it.

3.0 ENVIRONMENTAL TESTING

IRIF Test I-69 was carried out on a series of Tektronix pigments. The materials, the tests, test results and conclusions pertinent to this test are described.

3.1 Materials

Except for one IITRI pigment, all of the pigments tested in IRIF Test I-69 were obtained from Tektronix, Inc., Beaverton, Ore. through the courtesy and cooperation of Dr. Ralph Mossman. IITRI forwarded approximately ten (10) pounds each of SP-500 ZnO and anatase titania. Tektronix prepared these materials by first slurrying in distilled water at a 2.05 Zn/Ti mole ratio, by drying the slurry in a large spray-dryer, and then by calcining at various temperatures. Table 2 shows the materials returned to IITRI.

Table 2

Tektronix Pigments

Designations		Descriptions
IITRI	Tektronix	
T-1	J-1156-65	Spray-Dried, Unfired
T-2	J-1156-65A	Spray-Dried, Fired at 900°C/ 8hr.
T-3	J-1156-65B	Spray-Dried, Fired at 1200°C/ 1hr.
T-4	J-1156-65C	Spray-Dried, Fired at 1250°C/ 24hr.

Previous tests of these pigments, irradiated as powders, showed that T-1 was simply a mixture of ZnO and a-TiO_2; the spray-drying temperature was, however, sufficiently high to affect some conversion. In any case T-2 and T-3 pigments were obviously

superior, and further testing of T-1 was not justified. The purpose of the T-1 preparation was to have available a large quantity of the same precursor material used in the preparation of all the other T-series pigments.

3.2 IRIF Test I-69

In IRIF Test I-69 the samples were exposed to a total of 2660 ESH. The test was carried out using an A-H6 compact Hg-Ar illuminator at a solar factor of 6 (equivalent) UV suns under a maximum pressure of 2×10^{-7} Torr. Reflectance measurements were accomplished in the spectral range from 325 nm to 2600nm. These spectral scans were made under vacuum prior to UV irradiation, after 915 ESH, 2085 ESH and after 2660 ESH; a final scan was made after the system pressure was increased to 760 torr using pure O_2.

3.3 Materials and Test Results

The materials tested in IRIF I-69 are described in Table 3, wherein also are pertinent test results. The materials are grouped according to their descriptions in Table 2. The notation used in Table 3 is that which we have used consistenly to describe Zn_2TiO_4 pigments. A few examples however, may be of assistance in understanding the data. Under T-2, we have listed, for example, powder, "OI-650", ":k_2SiO_3 powder", and "-A-10/OI-650". In the same sequence, these descriptions refer to the T-2 pigment which was irradiated as a powder, as an OI-650 paint; to the T-2 pigment was potassium silicate encapsulated and then irradiated as a powder; and to the T-2 pigment which was acetic acid washed (for zinc oxide leaching), fired at 1000°C/2hr, and then dispersed in OI-650 resin.

Table 3

IRIF I-69
ULTRAVIOLET IRRADIATION TEST RESULTS

T-2 Pigments =	[1]R_{max}	[2]R_k	[3]ΔR_{400}	Solar Absorptance Values Initial	915 ESH	2085 ESH	2660 ESH	[0]$_2$ Bleach
Powder	90	38	0.14	.187	.196	.297	.300	
OI-650	89	31	0.11	.187	.182	.208	.236	
OI-650G	94	30	0.065	.312	.130	.140	.158	
:k_2SiO_3 powder	90	43	0.10	.166	.179	.185	.196	
:k_2SiO_3/OI-650G	94	28*	0.07*		.142	.146	.224	0.187
A-10/OI-650	82	72	0.08	.233	.229	.260	.267	
T-3 Pigments =								
OI-650	75	25	0.05	.318	.316	.325	.345	.343
:k_2SiO_3/OI-650	68	23	0.04	.372	.376	.386	.398	
-A-10 powder**	84	65	0.16	.210	.218	.233	.261	
-A-10/OI-650	74	62	0.08	.319	.326	.339	.362	.365
T-4 Pigment								
-A-10 powder	83	53	0.13	.224	.230	.299	.303	.298
IITRI Pigment								
LH-53(6-12)/OI-650G	65	32	0.15	.391	.385	.428	.429	

*Value in this instance is that after 915 ESH
**Sample was marred during testing; data somewhat doubtful

Notes

1. R_{max}, highest reflectance value in region 325 - 2600nm
2. R_k, reflectance at 370nm, the "knee" in the Zn_2TiO_4 spectra.
3. ΔR_{400}, the maximum induced reflectance change at 400nm.

The spectral reflectance curves are presented in Figures 7 through 18. Several of the significant features of these curves, in addition to solar absorptance values, have also been presented in Table 3. The column designated R_{max} indicates the highest reflectance of the unirradiated material in the spectral region 325 to 2600nm. The next column, R_k, lists the reflectance values of the unirradiated materials at 370nm. The significance of the "knee", which can be discerned from the reflectance curves below 375nm, as shown in Figures 7-18, rests in the fact that the "knee" reflectance relates to the amount of ZnO inclusion.

In the case of sample No. 6 (T-2:K_2SiO_3/OI-650G), an operator error caused the unirradiated material spectrum to be scaled improperly. Hence in this case, the analysis will rely primarily on the relationship of the "irradiated" spectra to one another. Other performance data, such as the ΔR at 900nm, were also studied, but they have not been listed because, in the case of these pigments at least, there has been no substantial "belly" damage, that is, reflectance losses of 5% or more. In fact, most materials suffered less than 2% reflectance loss in this region - a region in which sensitivity to surface defects or incorrect stoichiometry become strongly prominent.

3.4 Analyses and Discussions

As expected the Tektronix pigments demonstrate very good optical stability. In terms of induced solar absorptance change, they compare very favorably with the baseline (IITRI) pigment, LH-53(6-12), (Fig. 18) which sustained a change of 0.038 in 2660 ESH. The best paint tested was T-2/OI-650G (Fig. 9); not only did this material display the best stability, but it possesses the lowest solar absorptance, again demonstrating the inherent stability of Zn_2TiO_4/OI0650G paints.

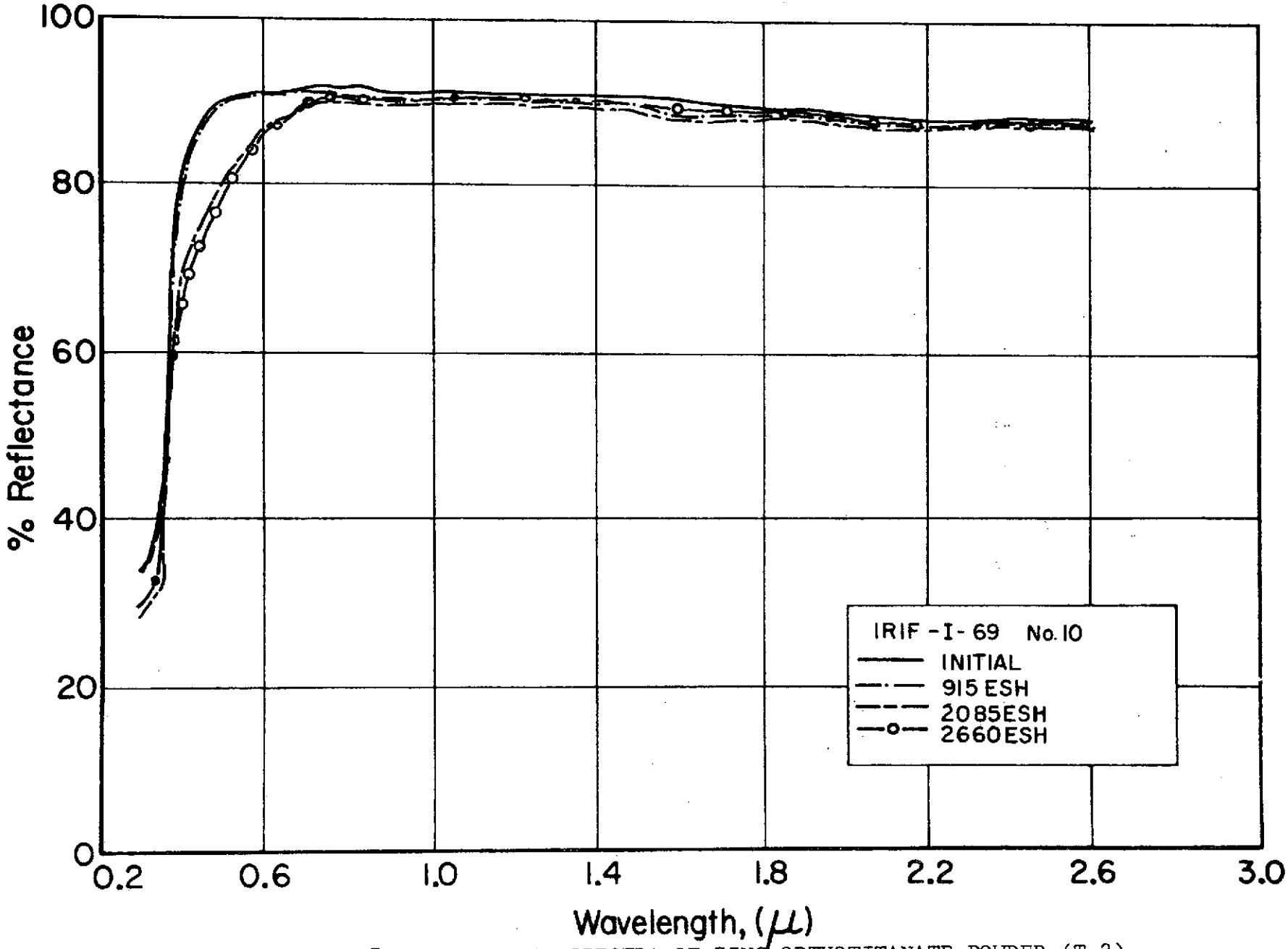


Figure No. 7 REFLECTANCE SPECTRA OF ZINC ORTHOTITANATE POWDER (T-2)

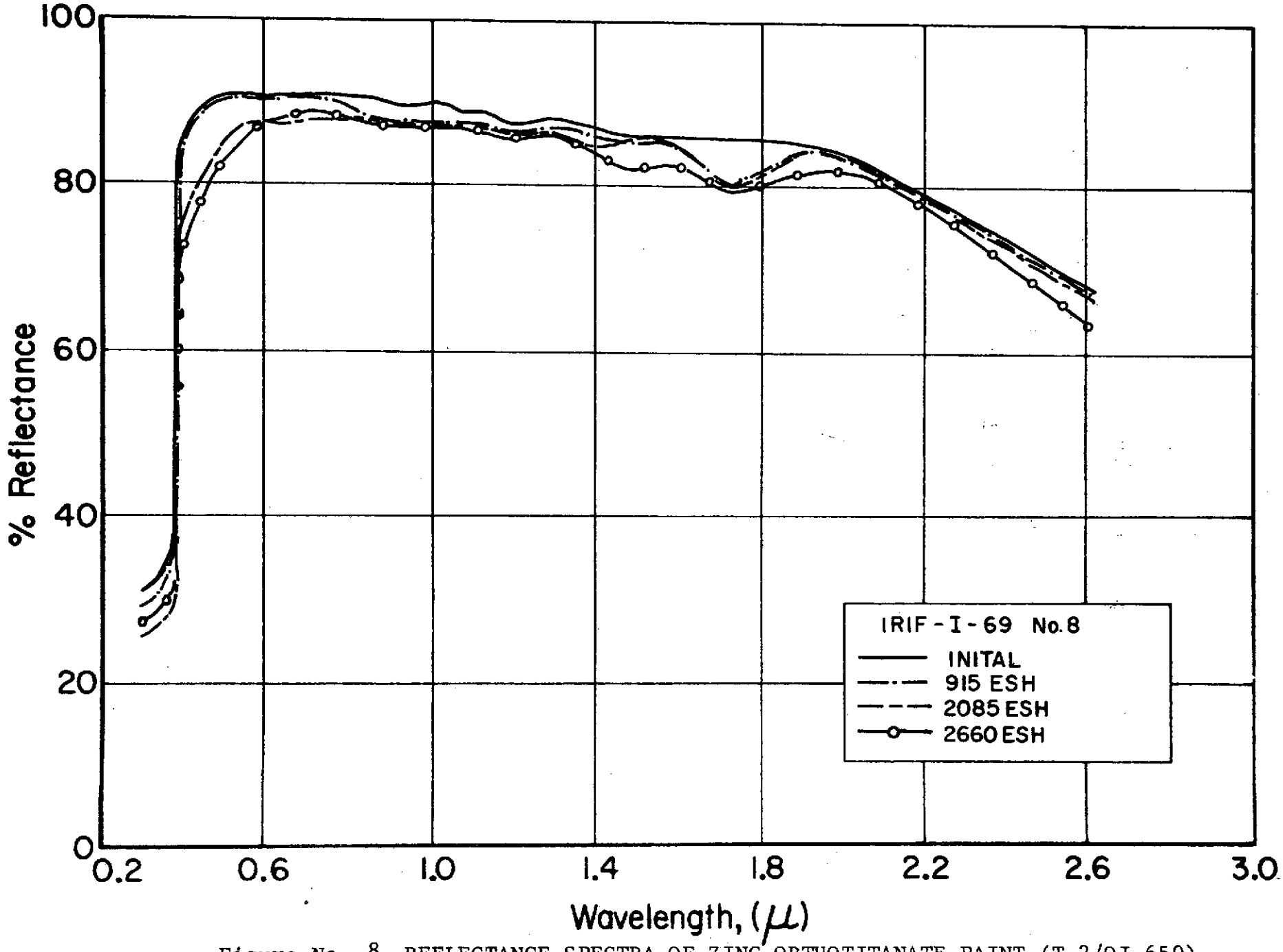


Figure No. 8 REFLECTANCE SPECTRA OF ZINC ORTHOTITANATE PAINT (T-2/OI-650)

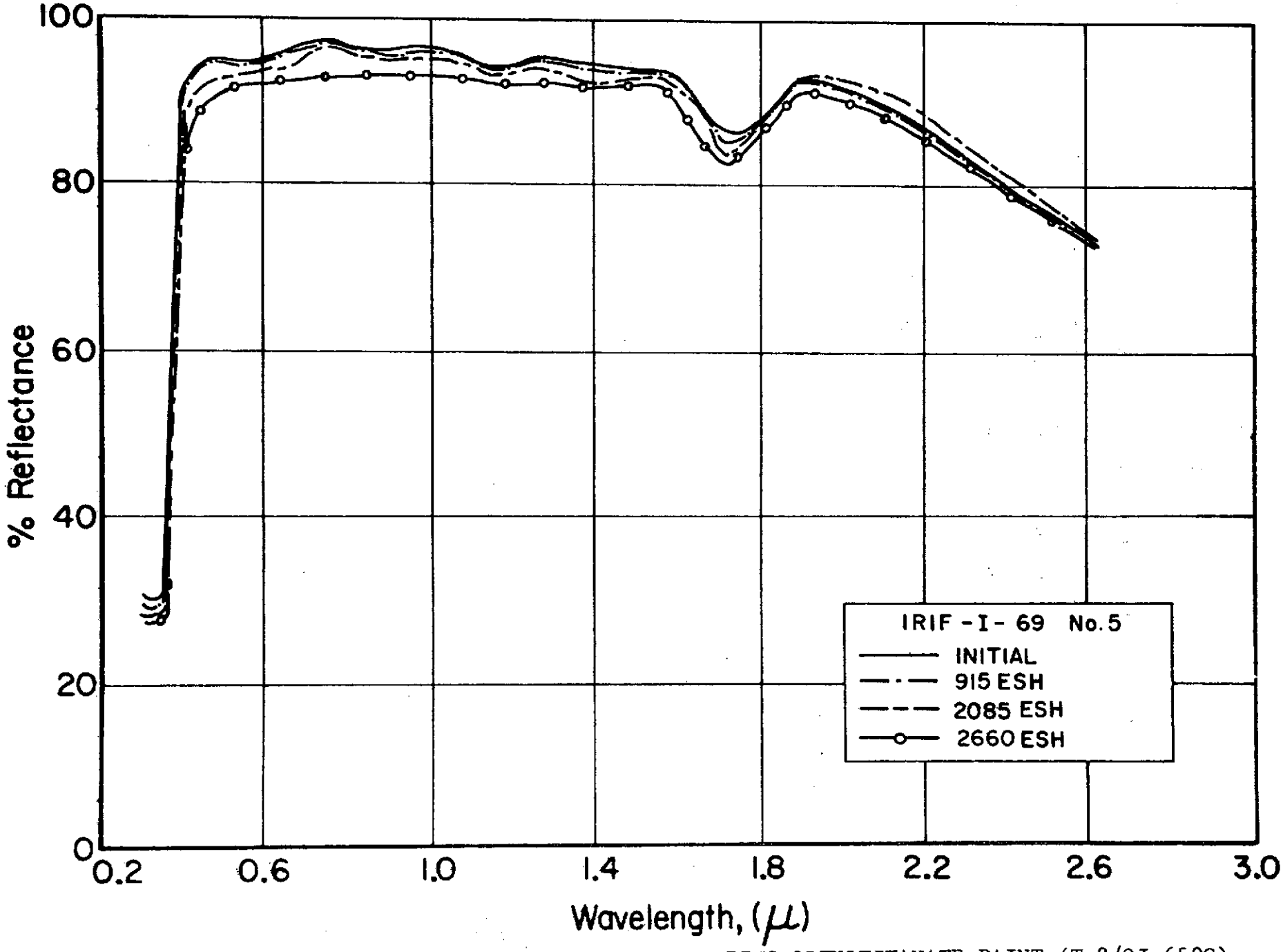


Figure No. 9 REFLECTANCE SPECTRA OF ZINC ORTHOTITANATE PAINT (T-2/OI-650G)

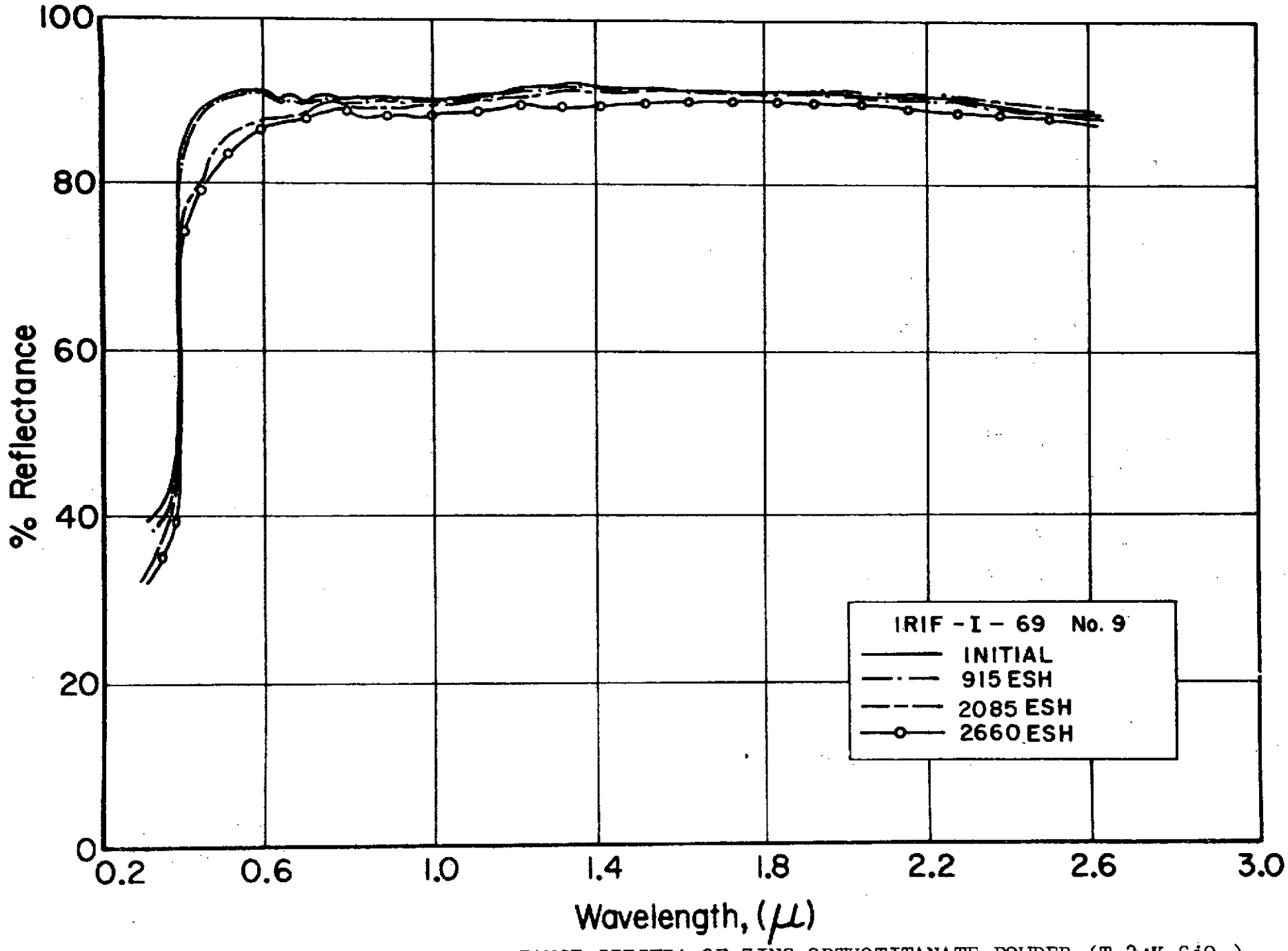


Figure No. 10 REFLECTANCE SPECTRA OF ZINC ORTHOTITANATE POWDER (T-2:K_2SiO_3)

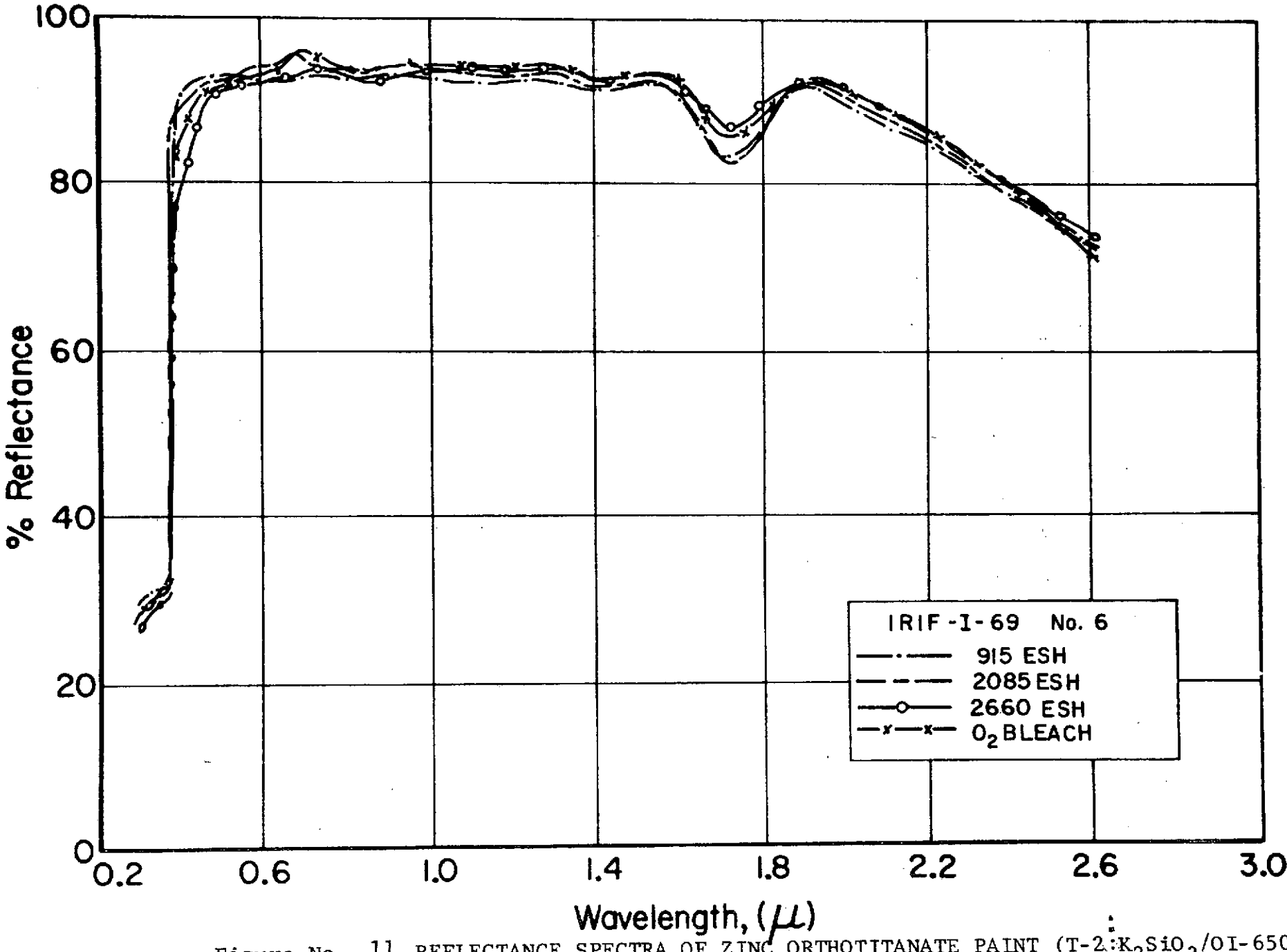


Figure No. 11 REFLECTANCE SPECTRA OF ZINC ORTHOTITANATE PAINT (T-2:K_2SiO_3/OI-650G)

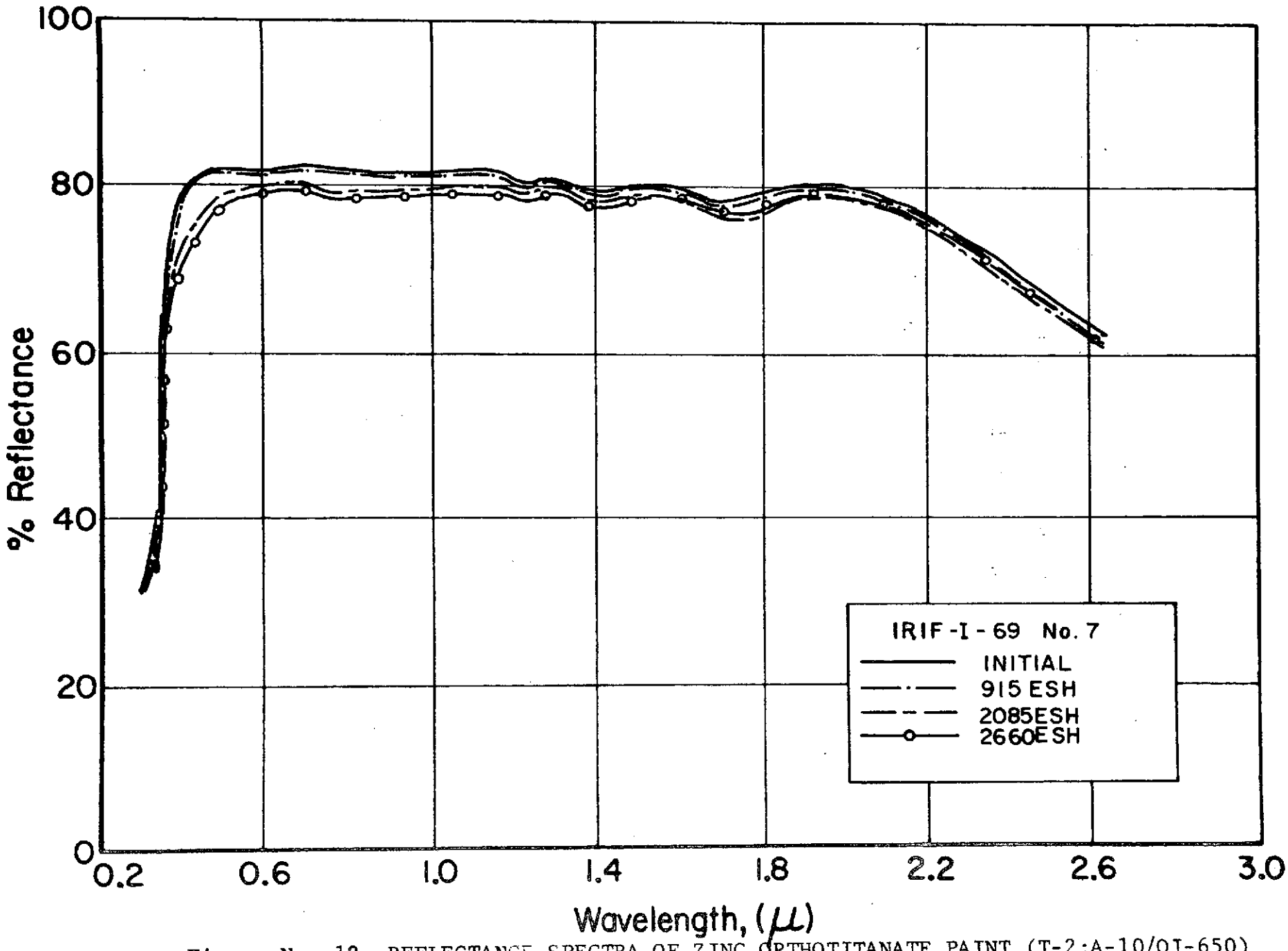


Figure No. 12 REFLECTANCE SPECTRA OF ZINC ORTHOTITANATE PAINT (T-2:A-10/OI-650)

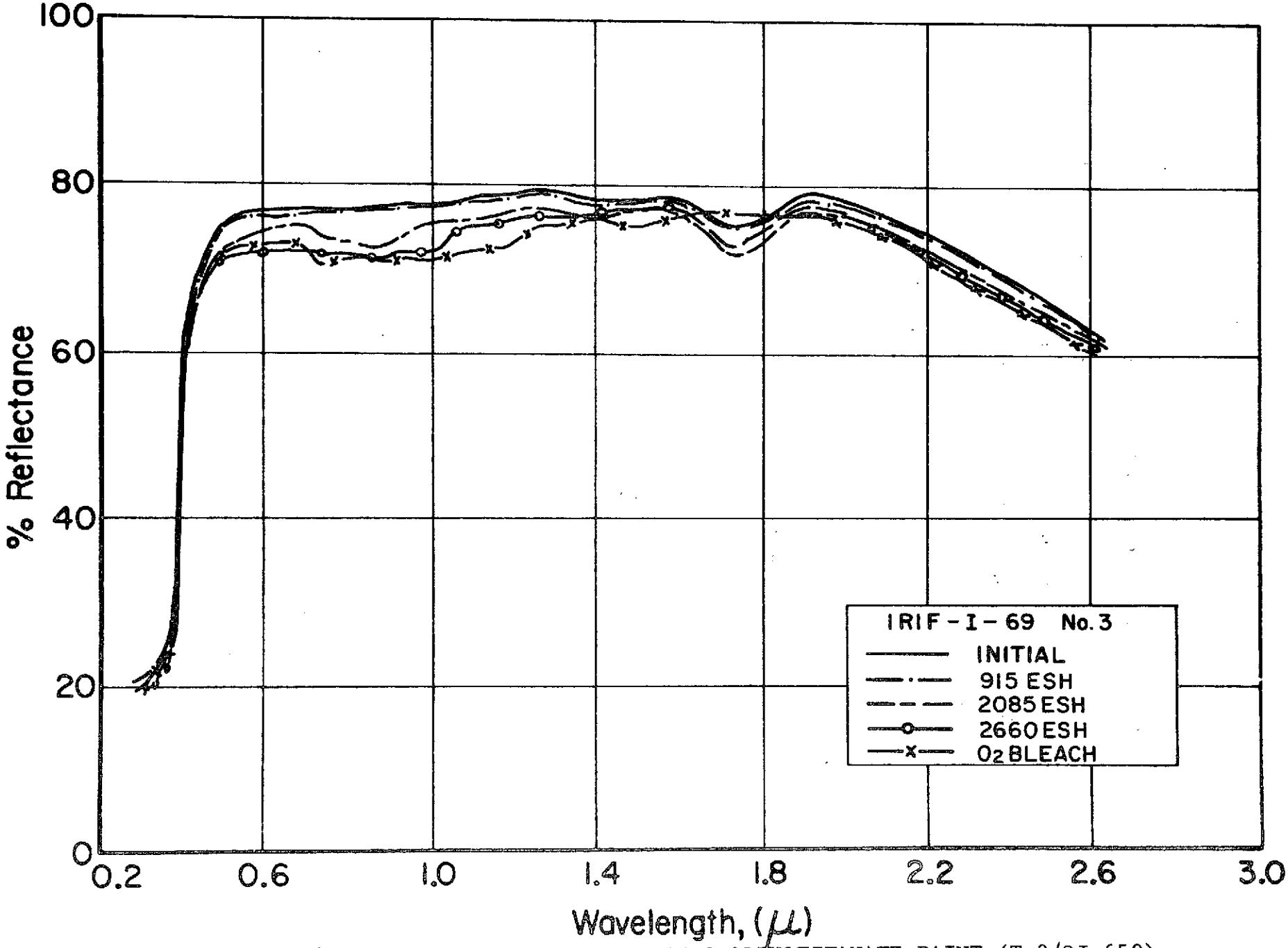


Figure No. 13 REFLECTANCE SPECTRA OF ZINC ORTHOTITANATE PAINT (T-3/01-650)

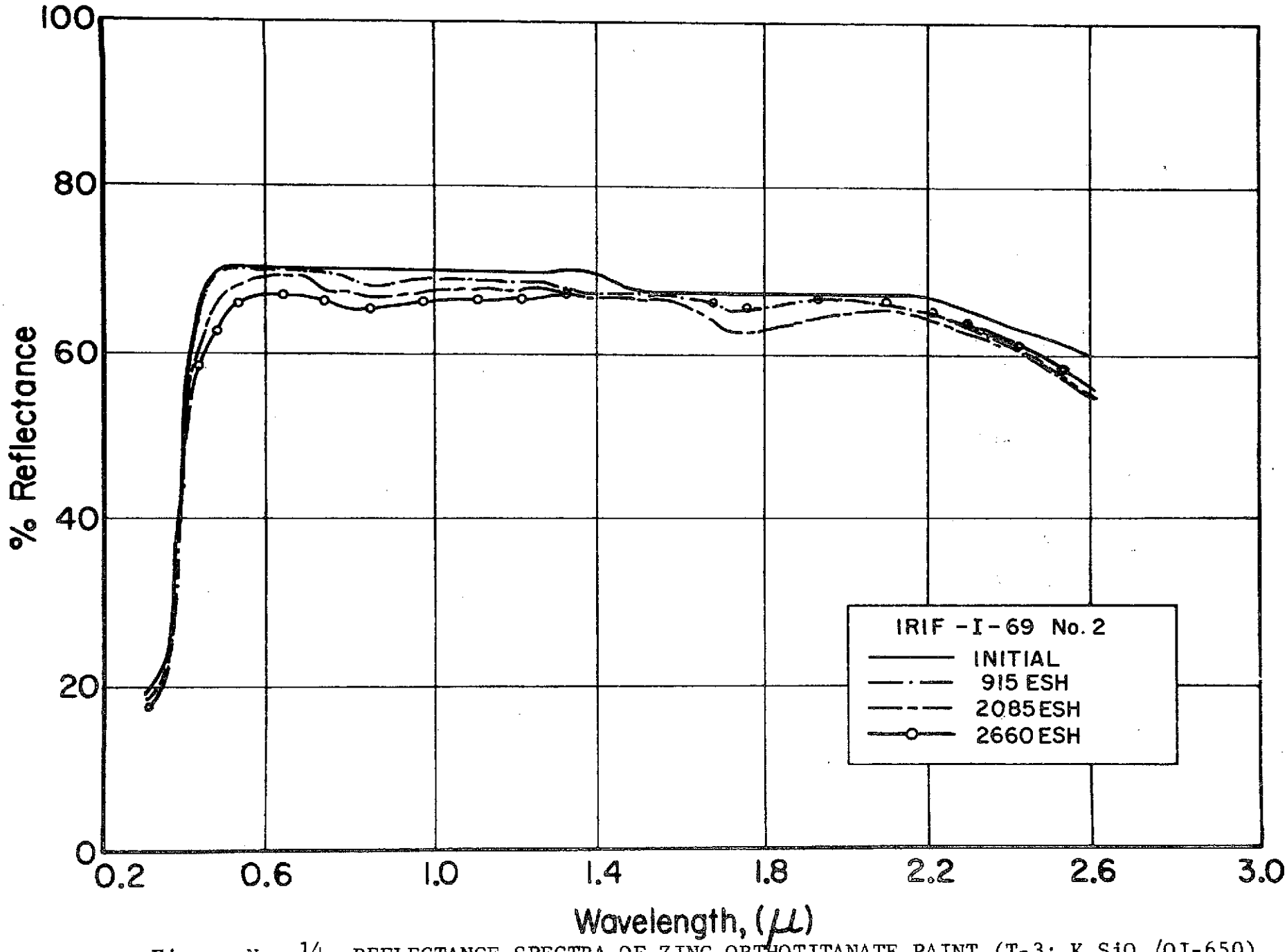


Figure No. 14 REFLECTANCE SPECTRA OF ZINC ORTHOTITANATE PAINT (T-3: K_2SiO_3/OI-650)

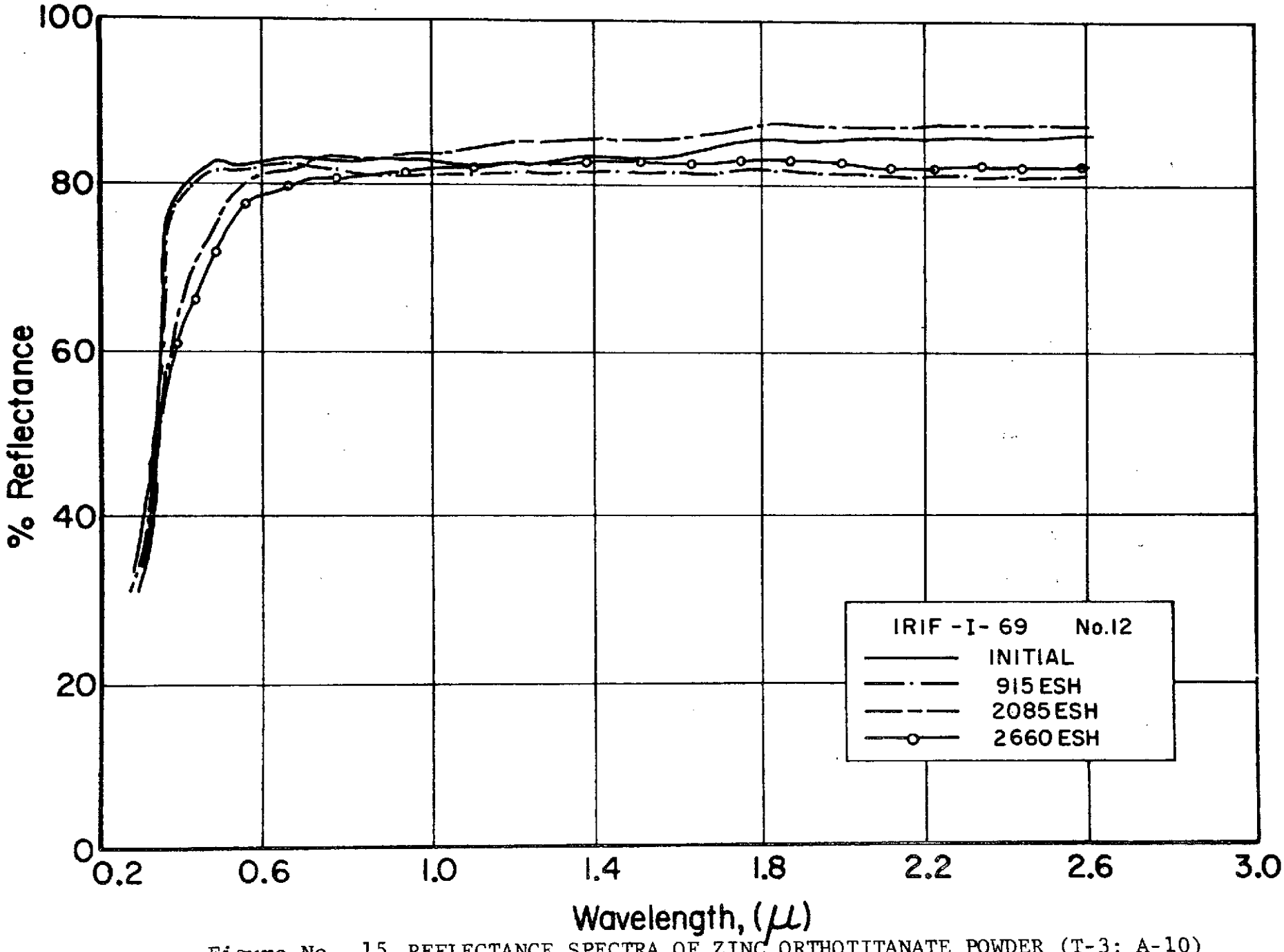


Figure No. 15 REFLECTANCE SPECTRA OF ZINC ORTHOTITANATE POWDER (T-3: A-10)

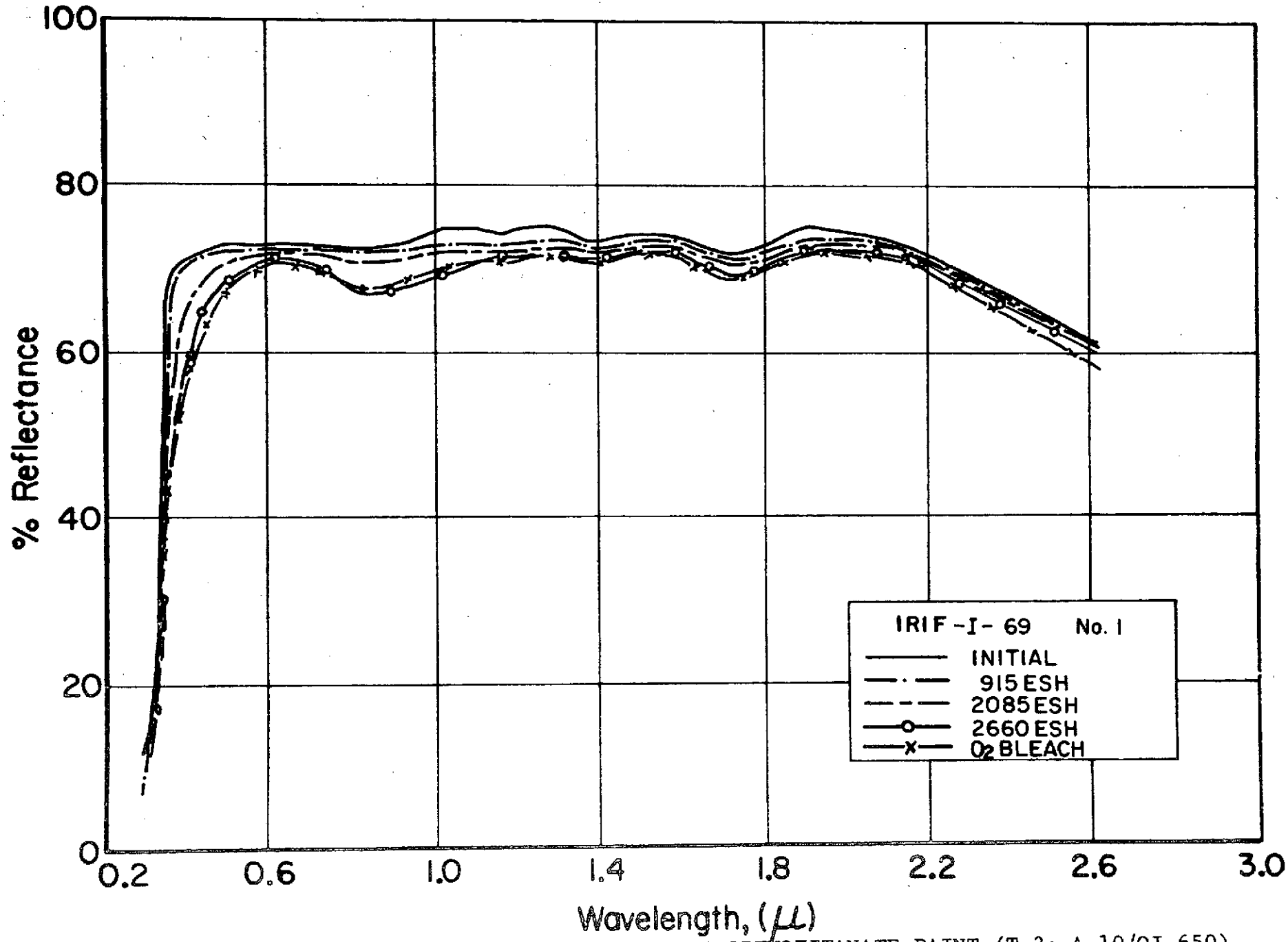


Figure No. 16 REFLECTANCE SPECTRA OF ZINC ORTHOTITANATE PAINT (T-3: A-10/OI-650)

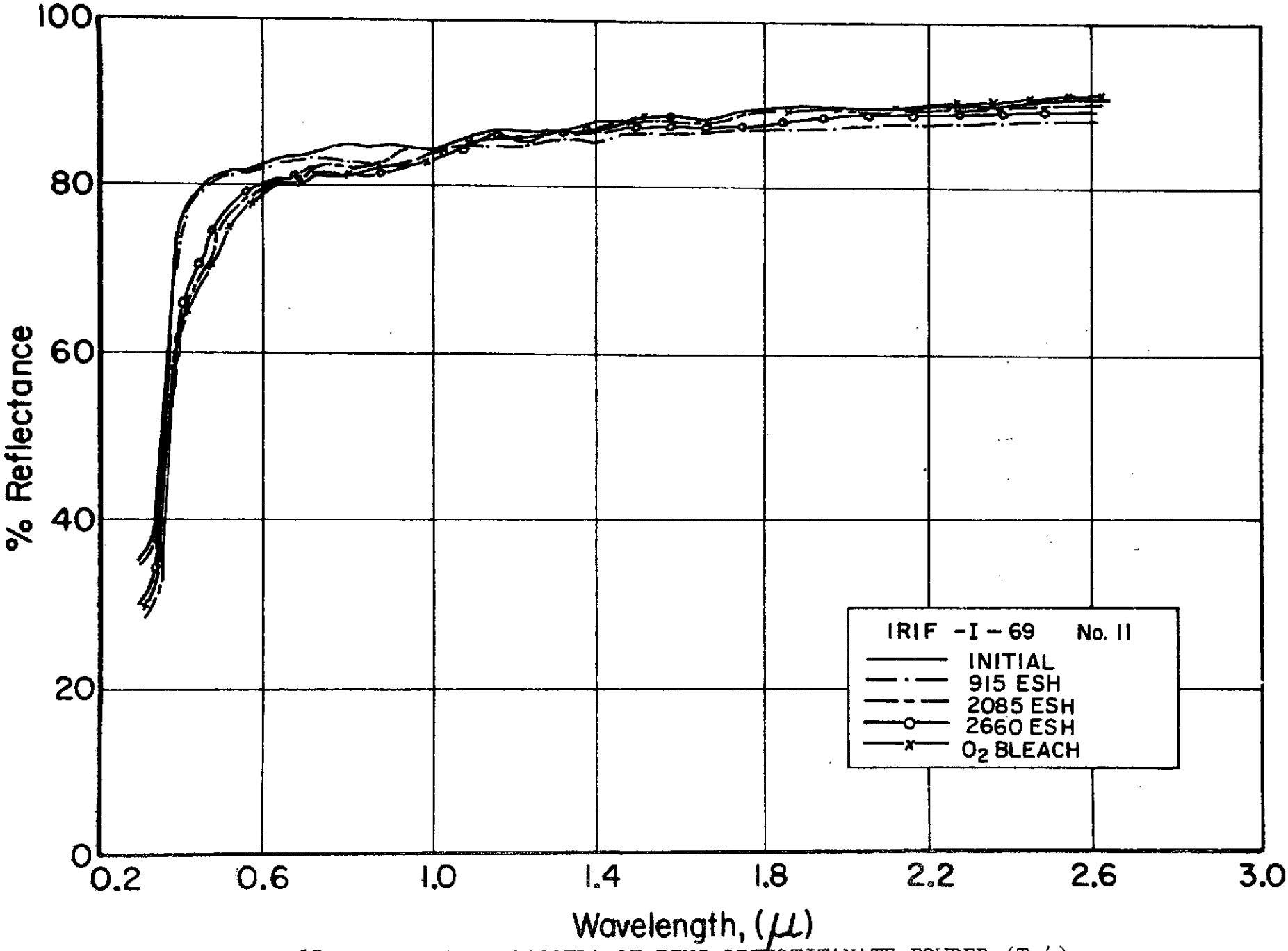


Figure No. 17 REFLECTANCE SPECTRA OF ZINC ORTHOTITANATE POWDER (T-4)

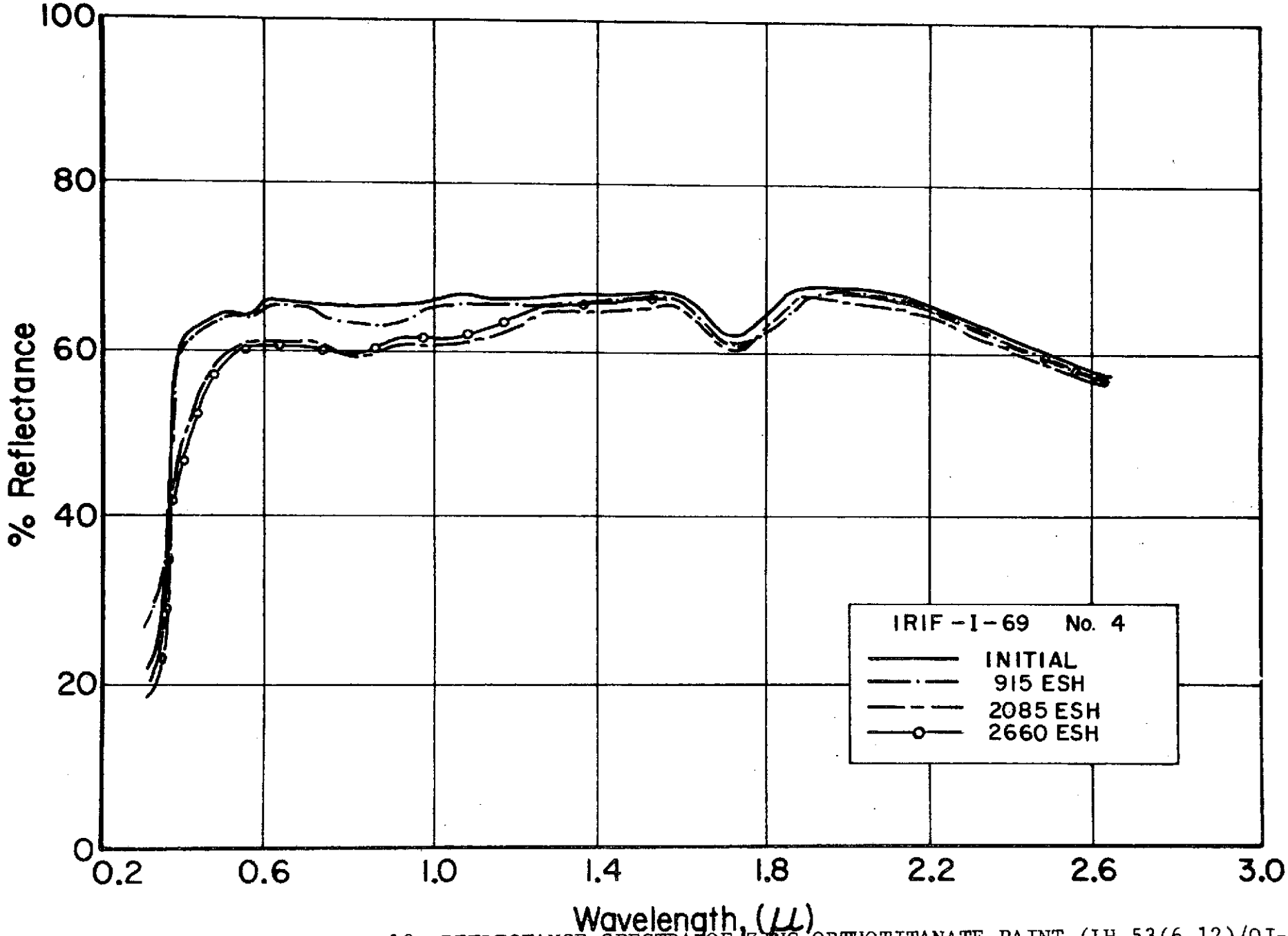


Figure No. 18 REFLECTANCE SPECTRA OF ZINC ORTHOTITANATE PAINT (LH-53(6-12)/OI-650G)

From tests such as these, however, we attempt to establish the parameters of the production process which lead to a pigment which is both optically stable and has high solar reflectance. In this case we have three temperature-time combinations 900°C/8hr (T-2), 1200°C/1hr (T-3), and 1250°C/24hr-(T-4). High reflectance is attained at 900°C, as well as good stability, in effect negating any advantage of 1200°C. It may be that an intermediate temperature might produce an even better pigment, particularly since T-4 pigments (1250°C/24hr) have not displayed as good stability.

The acid leaching and subsequent re-calcination at 1000°C/ 2hr. in every case enhanced the visible reflectance but did not substantially affect optical stability. The A-10 treatment therefore, remains as a reasonable approach to the improvement of α_s. The effectiveness of encapsulation of the pigments with K_2SiO_3, though this process is somewhat valuable in improving α_s, cannot be as easily determined, but in general encapsulation tends not to affect stability. This latter observation is true mainly because these particular pigments show little, if any, tendency to surface defect formation as evidenced by a reflectance loss in the 900nm region.

The test results support our conclusions that the Tektronix spray-dry process is a viable one, that it indeed can produce pigments at high production rates, (>10 lb/day), that the pigments so produced are inherently stable (or can be made so), and that the paints made from them are also sufficiently reflective and stable to allow us to consider this process a logical alternative to the current processes. This evaluation,

however, must be understood in proper perspective. These Tektronix pigments would require, as would pigments from any other candidate method, extensive testing and further development. These tests simply demonstrate that the method is clearly worth pursuit, but only if current methods are shown to be insufficient.

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